Voltage-Induced Infrared Spectra from Polymer Field-Effect Transistors

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Summary: Charge-induced infrared absorption spectra from the metal–insulator–semiconductor diodes fabricated with aluminum oxide, poly(p-xylylene), and SiO_2 as gate dielectric and regioregular poly(3-octylthiophene) as organic semiconductor have been measured *in situ* with reflection or transmission configurations by the FT-IR difference-spectrum method. The observed bands have been attributed to the carriers injected into the polymer layers under the application of minus gate bias. The wavenumber of the band around 1300 cm^{-1} depends on the gate voltage, indicating that the structure of the carriers depends on the carrier concentration. There exist upper limits in the concentrations of the injected carriers. *In situ* infrared absorption measurements provide the information about the injected carriers, which affect the properties and the functions of polymer field-effect devices.

Keywords: conjugated polymers; field-effect transistors; infrared spectroscopy; metal–insulator–semiconductor diodes

Introduction

Conjugated polymers have been incorporated as the active semiconductors in field-effect transistors (FETs).[1,2] Polymer FETs have the potential to provide an innovative low-cost technology for smart cards, radio-frequency identification, etc. through the solution-cast and inkjet-printing methods. Two common device configurations used in polymer FETs are shown in Figs. 1a and b. A polymer FET has three electrodes: source, drain, and gate. In a bottom-contact device (Fig. 1a), the source and drain electrodes are formed onto the gate insulator, and a thin film of a conjugated polymer is formed. On the other hand, in a top-contact device (Fig. 1b), a thin film of a conjugated polymer is formed on the gate insulator, and the source and drain electrodes are formed on the polymer layer by heat evaporation. In these FETs, carriers are accumulated by the application of a voltage between the gate and the source electrodes. This is called field-effect doping. Since these organic FETs have a metal–insulator–semiconductor (MIS) structure, they are called MIS-FETs. A metal–insulator–semiconductor diode shown in Fig. 1c is a central part of the MIS-FETs. The studies on MIS diodes can lead us to the understanding of the

 DOI: 10.1002/masy.200450102

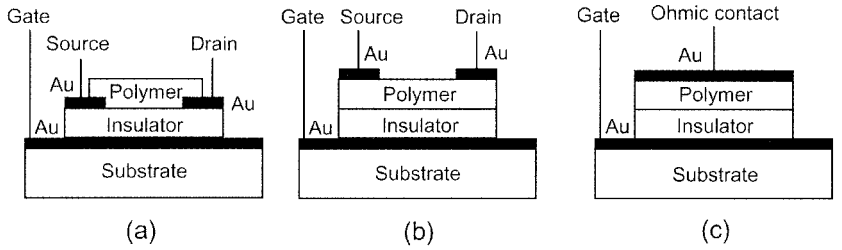

Figure 1. Polymer field-effect devices: (a) bottom-contact field-effect transistor; (b) top-contact field-effect transistor; (c) metal-insulator-semiconductor diode.

field-effect doping in the MIS-FETs. Important factors characterizing organic FETs are field-effect mobility and on/off ratio of the source–drain current. Shirringhaus *et al.*[3] reported the field-effect mobility of 0.1 cm^2/Vs for regioregular poly(3-hexylthiophene) (Fig. 2a), which is the highest value among polymer semiconductors. Various types of polythiophene derivatives,[4] poly(9, 9'-dioctylfluorene-co-bithiophene) (F8T2),[5] poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV),[6] etc. were also used as active semiconductors of FETs. Infrared spectroscopy is expected to give us information about the orientations of organic compounds, the interactions between organic compounds and metal electrodes, carrier injection, and carrier structure; these are important factors affecting the performance of organic FETs. In particular, the properties and the functions of organic FETs are strongly associated with the charge carriers generated in organic materials. We have demonstrated that *in situ* infrared reflection-absorption measurements are useful for investigating carriers in polymer LEDs and FETs in the

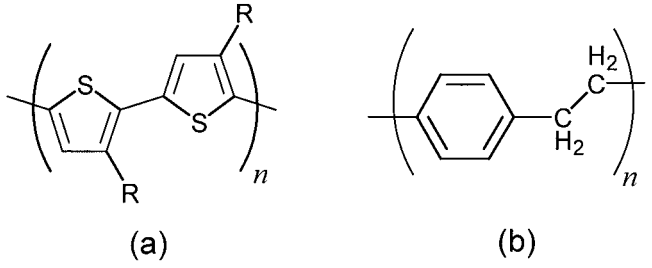

Figure 2. Chemical structures of (a) regioregular poly(3-alkylthiophene)s (P3AT): R = C_6H_{13}, poly(3-hexylthiophene) (P3HT); R = C_8H_{17}, poly(3-octylthiophene) (P3OT) and (b) poly(p-xylylene) (PPX).

previous papers.[7–9] In this work, we present the results of infrared studies on the three kinds of MIS diodes based on aluminum oxide, poly(p-xylylene) (abbreviated as PPX, Fig. 2b), and SiO_2 as gate insulator and regioregular poly(3-octylthiophene) (abbreviated as P3OT) as polymer semiconductor.

Experimental

Fabrication of MIS diodes

Regioregular P3OT was purchased from Aldrich. Three kinds of MIS diodes were fabricated as follows. (1) The MIS diodes with the Au/Aluminum oxide/P3OT/Au structure (called type I). Gold was thermally evaporated onto a glass substrate and used as gate electrode. Aluminum oxide was then sputtered onto this Au layer. The thickness of the aluminum oxide layer ranged between 250 and 300 nm. A film of P3OT was formed on the aluminum oxide layer by the spin-coating technique using a chloroform solution (0.8w%) of P3OT. A top electrode of Au was formed on the polymer layer by heat evaporation. (2) The MIS diodes with the Al/PPX/P3OT/Au structure (type II). Aluminum was thermally evaporated onto a glass substrate and used as gate electrode. A thin film of PPX (300 nm thick) was formed on the Al layer by chemical vapor deposition. A film of P3OT was formed on the PPX layer by the spin-coating technique. A top electrode of Au was formed on the polymer layer by heat evaporation. (3) The MIS diodes with the n^+-Si/SiO_2/P3OT/Au structure (type III). An *n*-silicon wafer (1–10 Ω cm, <100> axis, 525 μm thick) covered with a thermally grown oxide layers (310 nm thick) was purchased from Furu-uchi Chemical Co. Ltd. and used as substrate. The *n*-silicon was used as gate electrode. A film of P3OT was formed on the SiO_2 layer by the spin-coating technique. A top electrode of Au was formed on the polymer layer by heat evaporation. The bias dependence of the capacitance of the MIS diodes were measured on an Agilent Technologies 4263B LCR meter.

In the MIS diodes used for infrared measurements (Fig. 3a), a finger-shaped Au top electrode (Fig. 3b) was formed by thermal evaporation through a shadow mask. The width of each finger was 75 μm, and the distance between adjacent fingers was also 75 μm.

Infrared measurements

Infrared spectra were recorded on a Digilab FTS 7000 spectrophotometer equipped with an MCT detector. The infrared spectra of type I and II devices were measured by a

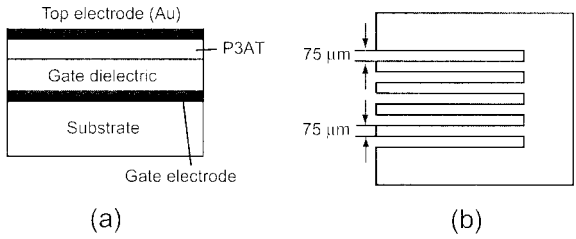

Figure 3. MIS diode with a finger-shaped electrode for infrared measurements.

reflection-absorption configuration with a single attenuated total reflection (ATR) accessory (Specac Golden Gate™). A home-made plate was used as the sample stage for an polymer MIS diode instead of the plate equipped with an ATR prism. The incident angle of this accessory was fixed to be 45 degree. Infrared light was incident on the ohmic contact of the device. A half of the incident infrared light passed through the polymer and the gate insulator layers and reflected by the Au gate electrode; the reflected light passed through the gate insulator and the polymer layers again. On the other hand, the other half of the incident light was reflected by the counter electrode. One should make a correction to the observed absorbance change ΔA^{obsd} to obtain real absorbance change ΔA^{real} induced by the application of the gate bias by using the following equation:[10]

$$\Delta A^{\mathrm{real}} \approx 2\Delta A^{\mathrm{obsd}}. \qquad (1)$$

The infrared spectra of type III devices were measured by a normal transmission absorption configuration.

Voltage-induced infrared spectra were measured by using the FT-IR difference-spectrum method. We accumulated the intensity spectrum B_{V} with the voltage of V and then the intensity spectrum $B_{\mathrm{V}'}$ with the voltage of V'. These procedures were repeated until a good-quality spectrum was obtained. The absorbance spectrum calculated from the observed B_{V} and $B_{\mathrm{V}'}$ intensity spectra corresponds to the difference between the infrared absorption spectra at the V and V' states, as shown the following equations.

$$\log\frac{B_{\mathrm{V}'}}{B_{\mathrm{V}}} = \log\frac{B_{\mathrm{R}}}{B_{\mathrm{V}}} \times \frac{B_{\mathrm{V}'}}{B_{\mathrm{R}}} = \log\frac{B_{\mathrm{R}}}{B_{\mathrm{V}}} - \log\frac{B_{\mathrm{R}}}{B_{\mathrm{V}'}} = A_{\mathrm{V}} - A_{\mathrm{V}'} = \Delta A \qquad (2)$$

where B_R is a reference intensity spectrum.

Results and Discussion

Characteristics of MIS diodes

The capacitance *versus* voltage (*C–V*) plots of MIS diodes are useful for checking that the MIS devices are charging properly. The *C–V* plot of an MIS diode fabricated with aluminum oxide and P3OT (type I) is shown in Fig. 4. The abscissa denotes the potential of the gate electrode with respect to the top electrode. The observed curve is similar to that of the MIS diode fabricated with regioregular P3HT.[9,11] The observed curve is characteristic of an MIS diode based on a *p*-type semiconductor.[12] When a negative bias is applied to the gate electrode with respect to the top Au electrode, positive carriers are accumulated at the polymer–insulator interface. In the negative bias region of the *C–V* curve, capacitance shows a plateau at a high value of 39 nF cm^{-2}. In this region, the observed capacitance is attributable to the aluminum oxide layer. When the capacitor consists of the gate insulator, and a carrier has charge e or $-e$ (e, elementary electric charge) , the induced carrier sheet density N_C under the voltage V can be expressed as

$$N_C = \frac{Q}{eS} = \frac{CV}{eS} = \frac{\varepsilon_r \varepsilon_0 S}{d} \times \frac{V}{eS} = \frac{\varepsilon_0}{e} \varepsilon_r E \qquad (3)$$

where ε_0 is the vacuum permittivity, and ε_r, d, S , and E are the dielectric constant, thickness, active area, and electric field of the gate insulator layer. Thus, the carrier density is proportional to the product of ε_r and E. In the positive bias region, capacitance shows a

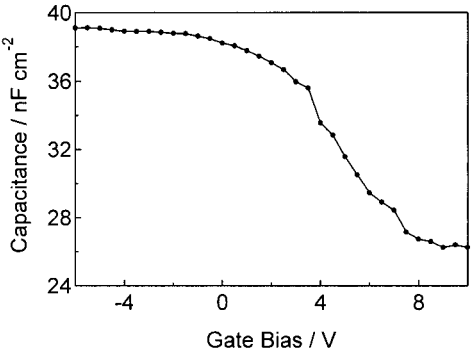

Figure 4. *C–V* plot of an MIS diode with the Au/aluminium oxide (250 nm thick)/P3OT/Au structure measured at 1 kHz.

low value. In this region, carriers are not accumulated. The observed capacitance originates from the direct series of the P3OT and the aluminum-oxide capacitors. A material having a high dielectric constant facilitates the carrier accumulation in the transistor channel at much lower electric fields. The dielectric constants of some gate dielectrics reported in the literature are listed in Table 1.

Table 1. Dielectric constants of some gate dielectrics

materials	ε_r	materials	ε_r
SiO_2	3.9	poly(*p*-xylylene)	2.7
Si_3N_4	6.2	parylene C	3.2
Al_2O_3	10	polyimide	3.5
Barium zirconate titanate (BZT)	17	poly(4-vinylphenol)	3.6
Ta_2O_5	21		

Infrared measurements

Voltage-induced infrared difference spectra from an MIS diode based on aluminum oxide and P3OT (type I) are shown in Fig. 5. The observed spectrum in Fig. 5a is the difference spectrum between –5 and 5 V. The positive bands are attributed to the species generated at –5 V. The positive bands observed in Figs. 5b, c, d, and e can be ascribed to the species generated at –10, –20, –30, and –40 V, respectively. The observed voltage-induced infrared bands are attributed to the carriers (positive polarons) injected into the P3OT layers, because the observed infrared spectra are similar to $FeCl_3$-doping induced one (not shown). A P3OT film doped with $FeCl_3$ give rise to two electronic absorptions at 1.57 and ca. 0.5 eV; these bands can be assigned to positive polarons.[13] In the previous paper,[9] it has been demonstrated that the voltage-induced infrared absorption from the MIS diode fabricated with P3HT is attributable to positive polarons. A positive polaron has charge $+e$ and spin 1/2. The charge and spin are localized over several repeating units of a polymer chain with structural changes. Polarons show characteristic infrared-active vibrations (IRAVs), because of their structural changes. As the absolute value of the bias voltage increases from Fig. 5a to e, the carrier sheet density increases (see equation (3)). As the absolute value of the bias voltage increases, the wavenumber of the infrared band around 1300 cm^{-1} shows an upward shift from 1273 to 1331 cm^{-1}, as shown in Fig. 5. This band may be largely contributed by the effective-conjugation coordinate proposed by Zerbi and his co-workers.[14] According to the effective-conjugation coordinate theory, the observed

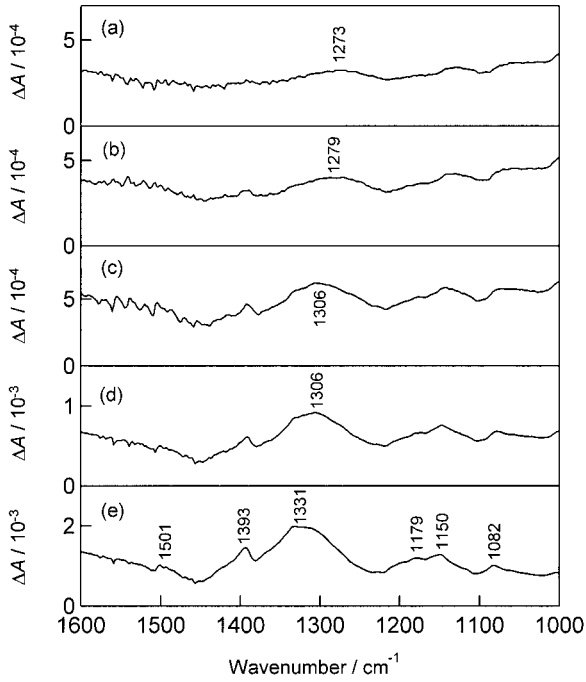

Figure 5. Gate-bias dependence of voltage-induced infrared absorption from a Au/aluminium oxide/P3OT diode (type I): (a) –5 Vminus 5V; –10 V minus 10V; –20 V minus 20 V; –30 V minus 30 V; –40 V minus 40 V.

upward shift is attributed to the shortening of effective conjugation length associated with injected charges (polarons) with increasing carrier sheet density.

In the infrared spectrum of a n^+-Si wafer with oxide layers (500 nm thick) on its both surfaces, a strong band is observed at 1094 cm^{-1}. This band is ascribed to the SiO stretching vibration of silicon oxide. It seems to us that infrared light does not transmit a glass substrate whose major component is SiO_2. However, infrared light can pass through the n^+-Si wafer, because the thickness of the SiO_2 layers is thin. Thus, the charge-induced infrared spectra from the MIS diodes fabricated with SiO_2 and P3OT (type III) have been obtained by a normal transmission-absorption configuration. The observed bands are also attributable to positive polarons. The charge-induced infrared spectra from the MIS diodes based on PPX and P3OT (type II) have been obtained by reflection-absorption

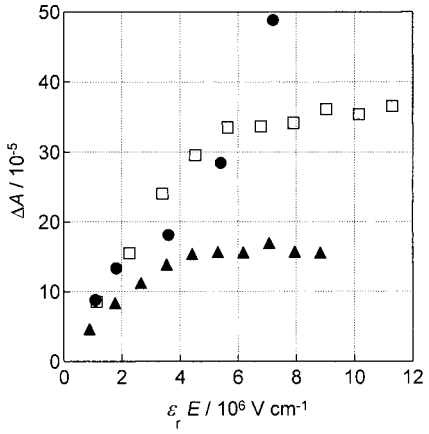

Figure 6. Relation between observed infrared intensities of the bands around 1300 cm^{-1} and $\varepsilon_r E$: ●, aluminium oxide; □, SiO_2; ▲, PPX.

configuration. The observed infrared bands are attributable to positive polarons. The observed intensities of the infrared band around 1300 cm^{-1} are plotted against the product of ε_r and E in Fig. 6; this quantity is proportional to the carrier sheet density, as shown in equation (3). The equation (3) indicates that the observed infrared intensity is proportional to the number of injected carriers. However, there exist upper limits in the observed intensities (*i.e.*, the numbers of injected carriers) for the MIS diodes based on SiO_2 and PPX. At each value of $\varepsilon_r E$, the observed infrared intensity for the PPX device is lower than those for the aluminum-oxide and the SiO_2 devices. These results probably originate from the existence of the surface states and the charges in the gate insulator layers. The MIS diode based on aluminum oxide has been destroyed at about 14×10^6 V cm^{-1} of $\varepsilon_r E$.

Conclusions

We have measured charge-induced infrared absorption from MIS diodes fabricated with regioregular poly(3-octylthiophene) by using the FT-IR difference-spectrum method. The infrared absorptions due to positive polarons (carriers) injected into the polymer layers have been obtained. The structure of polarons depends on the concentrations of injected polarons. There exist upper limits in the sheet densities of injected polarons for the MIS devices based on SiO_2 and poly(*p*-xylylene). It has been demonstrated that infrared spectroscopy is a powerful tool for investigating carriers induced by field effect.

Acknowledgments

This work was supported in part by the 21COE "Practical Nano-Chemistry" and the Grant-in-Aid for Exploratory Research (No. 14654137) from the Ministry of Education, Culture, Sports, Science, and Technology, and the Individual Research of Waseda University Grant for Special Research Projects (No. 2003A-571).

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